Magnetite utilisation for purging the industrial waters polluted by heavy metals

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Abstract. Seeing that water is a foremost environmental factor, its pollution is a topical problem, with serious consequences upon the health of the population and of the entire ecosystem, in general. Unlike part of the organic contaminants, the heavy metals are not biodegradable, therefore they tend to get accumulated in the living organisms. The heavy metals are extremely toxic, causing the inhibition of the cellular enzymatic processes or some other physiological disturbances. Certain industrial processes, such as the electrochemical coverage one, bring forth high concentrations of heavy metals in the discharged wastewaters. The paper sets out an innovating technology of purging the wastewaters derived from the galvanic covering processes. The high concentration of heavy metals in the wastewaters has caused the water purging process to be carried out in two stages. The former treatment stage includes such processes as pH adjustment, water oxygenation, electrochemical treatment, coagulation-flocculation and decantation. Since the concentration of the heavy metals in the water resulted from the first purging stage is higher than the maximum concentration allowed by the effective rules pertaining to the used industrial water discharge (as it cannot even be reused within the process), resorting to an advanced purging stage is called for. This one involves the utilisation of magnetite nanoparticles for adsorbing the metals at their surface and retrieving the magnetite-metal concentrated sludge, which is recirculated. The process is unfolded in multiple cycles and in the final stage the metals are removed from the magnetite by washing. The separation of the magnetite-metals solid phase from the water takes place in a magnetic module, where a solenoid fed by an electricity source generates a magnetic field. The magnetite-metals sludge gets agglomerated in the areas where the gradient of the magnetic field caused by the solenoid exceeds a threshold value, which can be reached by feeding the solenoid with continuous pressure of a certain value or with alternative voltage on a 0…500 Hz frequency range. The numerical shaping laid down in the paper for the magnetic module fed with direct and alternating current by using the COMSOL Multiphysics environment, shows the areas of agglomeration, being a useful instrument for designing the module at the industrial scale.

Key Words: wastewater treatment, electrochemical treatment, magnetite, metals, pre-oxidation.

Introduction. The wastewaters derived from the manufacturing (galvanisation) process are stored in a 30 m^3 stainless steel tank. In order to be continuously reused for washing the parts, the water in this tank must have a neutral pH (6.5-8) and the concentration of the dissolved substances (metals, oxides, salts, organic substances) must not exceed the values imposed for an industrial water.

In order to reuse this water within the manufacturing process, one has designed a water treatment flow able to provide the pH correction, the oxidation of the metals and of the dissolved organic substances, as well as their coagulation and flocculation for retention purposes, by precipitation, in a thin plate clarifier (www.businesswire.com) (Figure 1). After the clarification, the substances dissolved in the water are retained for a new treatment stage – by adsorption on the surface of the particles with magnetic properties inserted into the water, which afterwards are retained in a magnetic field, such particles being reused and periodically washed up. The sludge deposits in the thin plate clarifier, which are rich in metal oxides and salts, are stored in a sludge tank, from which they are taken over by the pump of a big bag filter for thickening the sludge (by extracting the solid substance from the sludge), the solid mass, i.e. the big bags, is stored in a container and the resulted water is re-circulated.

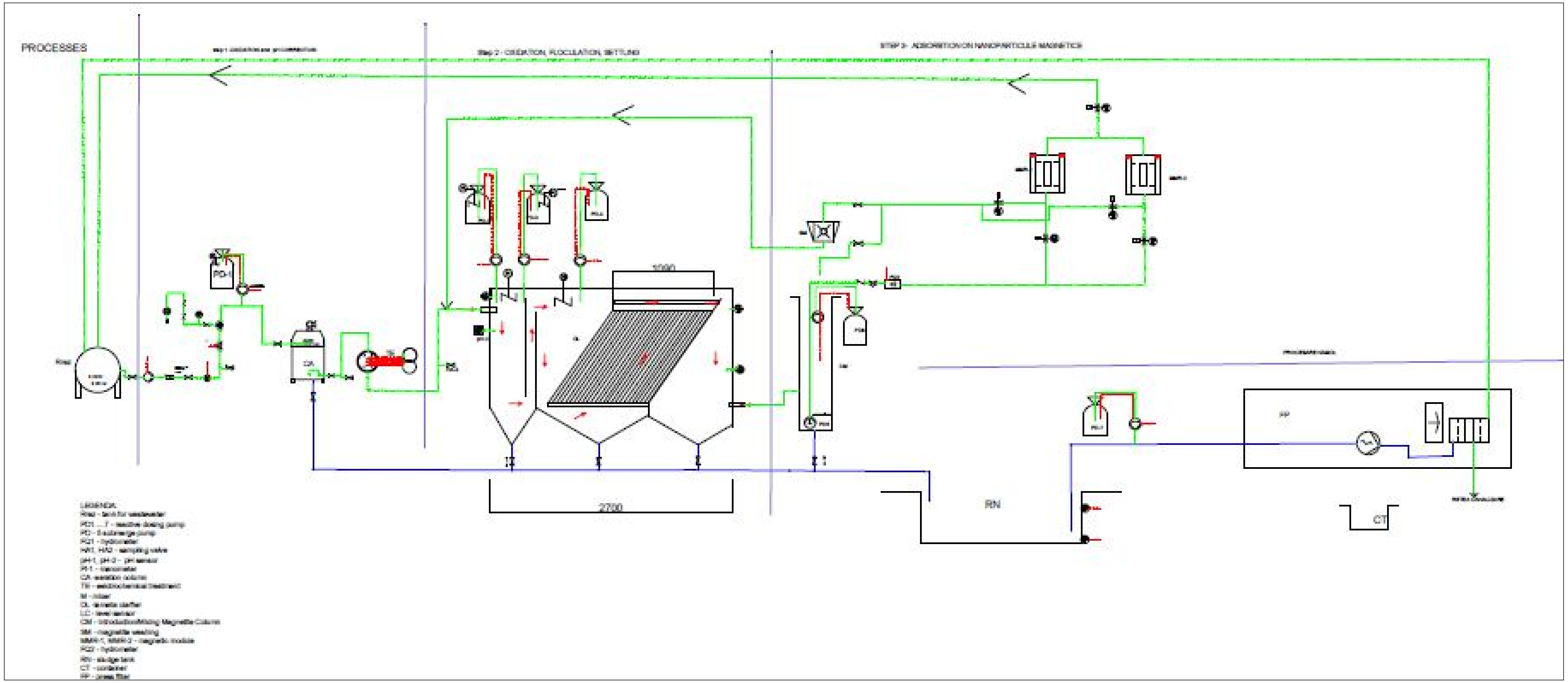

Figure 1. Drawing of the flow for purging the water derived from the galvanisation process.

Presentation of the magnetic module for separating the magnetite in the water. The magnetite, under the solid form of nanometric-sized granules, is inserted into a tank complete with an agitator for preparing the magnetite solution in the water. From this tank, the magnetite solution is taken over by a dosing pump and sent into a column with an emerged pump for entraining the water by the magnetic module (www.intechopen.com).

The magnetic module that separates the magnetic particles in the water is composed of two sub-modules wired in parallel – one running and the other one in the 'WASHING' (magnetite retrieval from the water) phase. The running cycle begins by a waiting phase, followed by the reverse washing and the magnetite retrieval. Thus, in the sub-module within the 'FILTERING' phase the water with the magnetite circulates in an ascending way (upwards). As for the magnetite particles, in order for them to be retained, the condition 1 has to be met :

$$\vec{F}_{MAGNETIC} + \vec{F}_{WEIGHT} \geq \vec{F}_{VISCOSITY} + \vec{F}_{DINAMIC\ PRESSURE} \qquad (1)$$

The magnetic module consists in two vertical sections of steel pipe – outer diameter Φext = 143 mm and wall thickness : 5 mm – with a low content of carbon. These sections are joined to the hydraulic circuit by flanges having got the nom. diam. 125 and the nom. press. 10. As a continuation of the flanges for joining the two columns there are steel reducing pieces until the 32 mm (1+1/4 inch) diameter. Each vertical section has a solenoid-shaped coil, whose central magnetic core is made of steel-silicon and which, in its upper part, is supported by a steel baffle where there are four passing holes for the water (Figure 2). In order to cause the appearance of the magnetic field that could retain the particles of magnetite to whose surface the metal particles dissolved in the water adhered, the solenoid emerged in the water is supplied by electrical power. The magnetite powder is composed of Fe_3O_4 micro-crystals, which do not have their own magnetic field, as they get magnetised in the presence of an exterior magnetic field, therefore the solenoid may be supplied by alternative current as well, without causing the attraction forces of the magnetite in a magnetic field to change course, according to the following relations 2 to 4 (http://people.ee.ethz.ch).

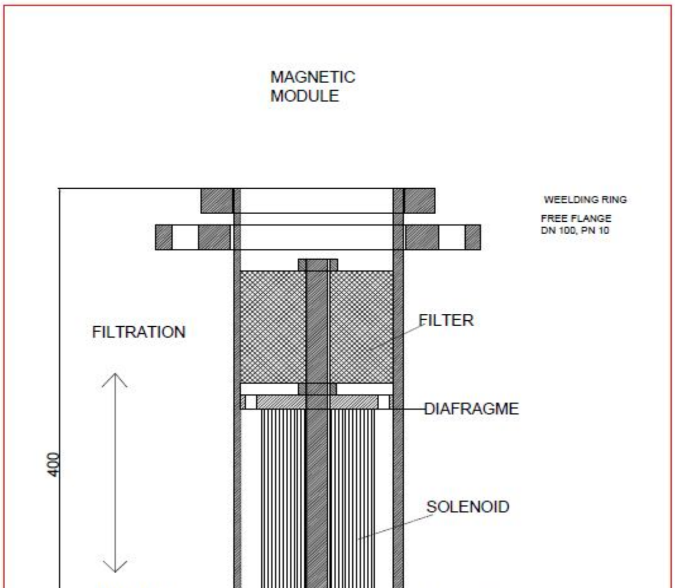

Figure 2. Theoretical drawing for the magnetic module.

In each point inside the magnetic module, the magnetic field can be expressed as:

$$H_x(t) = H_x \sin(\omega t) \quad (2)$$

where ω = 2πf, f being the supplying frequency for the inductor.

The energy of the magnetic field is defined as :

$$W_x = \frac{1}{2}\mu_0 H_x{}^2 \quad (3)$$

and the generalised forces that come up due to the field gradient are calculated by means of relation (4), which does depend on the direction of the magnetic field, as the latter one is square-expressed.

$$X_x = -\frac{\partial W_x}{\partial x} \quad (4)$$

By supplying the solenoid with alternative voltage (current), in time its ferromagnetic parts do not get magnetised permanently, so that upon the current interruption the magnetic field disappears and the magnetite can be removed from the module by reversing the water flowing direction.

Another advantage of supplying the solenoid by alternative voltage is the fact that under the action of the pressure differences and of the alternative magnetic field, the particles of magnetite display a microscopic vibration movement, which helps to efficiently capture the metals dissolved in the water. The alternative voltage/current for supplying the solenoids – the module 1 or the module 2 – is provided by a single-phased inverter, whose exit induces a maximum voltage of 230 V at a 500 Hz frequency.

Magnetic module modelling. As one can see in Figure 3, for the 1.5 m^3/h water flow rate, the maximum speed of the water in the magnetic module does not exceed 0.35 m/s, namely below the 0.7 m/s value, which no longer allows the magnetite to get agglomerated under the action of gravity. The programme runs for various input flow rates – from 0.5 m^3/h to 3 m^3/h – with an aim to check the flowing speeds in each point of the magnetic module and in order to simulate the areas of the magnetite agglomeration under the action of the gravitational field. Modelling took place in two dimensions (2D), with a view of obtaining a simple suggestive model, however it may be made in space, too (3D).

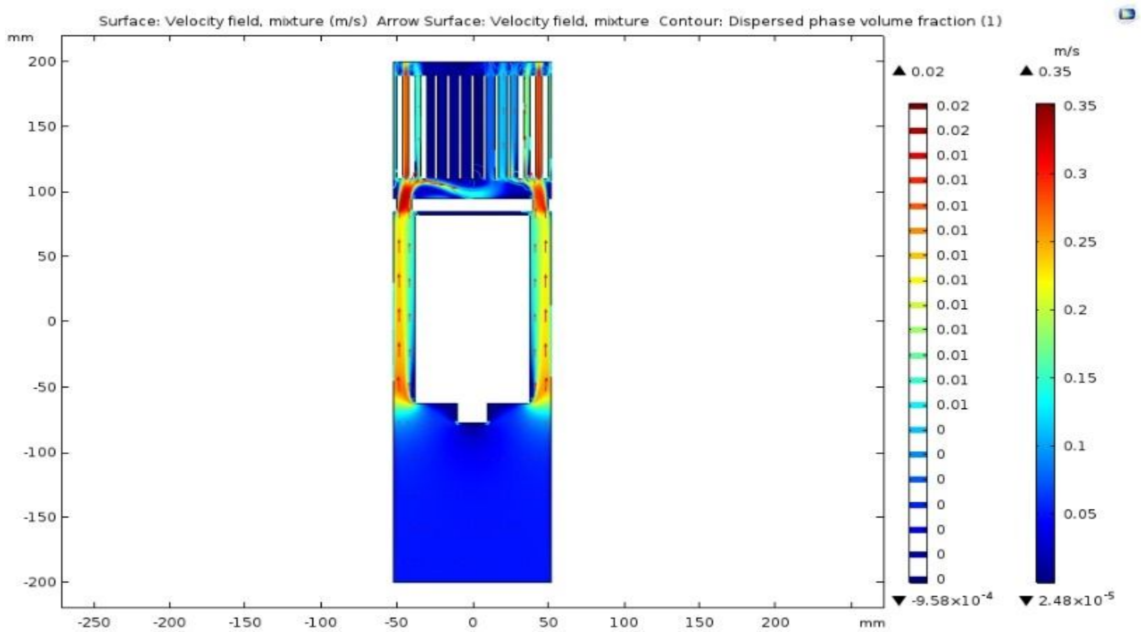

Figure 3. The simulation of the water flowing rates in the magnetic module, obtained by means of the COMSOL software.

The simulation of the magnetic field inside the magnetic module for the magnetite separation is set out in Figure 4 (the magnetic induction B), when the current intensity reaches its peak (the amplitude = 1.4 A).

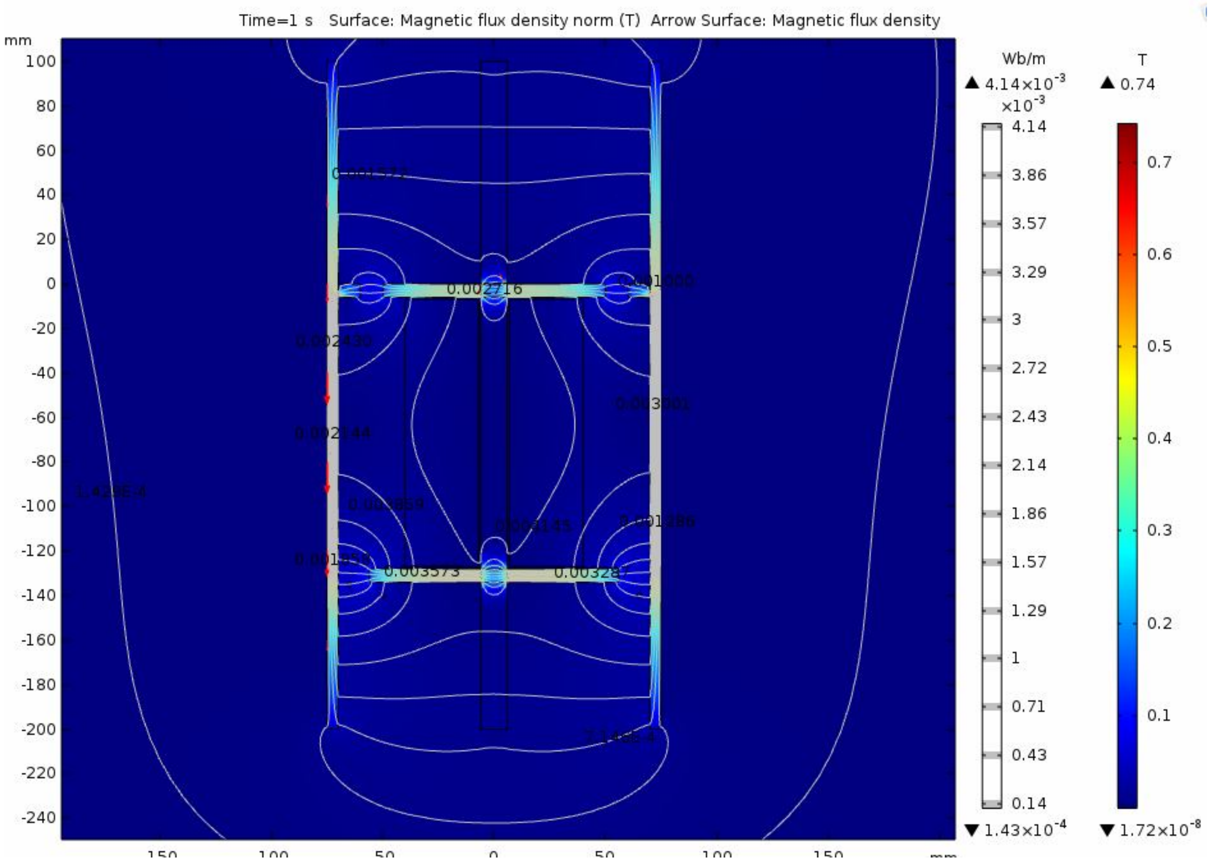

Figure 4. The intensity of the magnetic flow inside the magnetic module.

As it can be noticed in Figure 4, the gradient of the magnetic energy, that is the magnetic force, is more intense towards the ends of the solenoid (coil), where the field lines are more frequent. In these areas, as the magnetic force is more intense, it causes the magnetite to get agglomerated toward the inside of the magnetic module.

The modelling of the magnetic module may also take place in the MATLAB platform – the PDE mode, which has got the magnetic field solving forces implemented. The same set up (entered) values return the same results to the programme. The model of the magnetic module designed in space (3D) is laid down in Figure 5.

The entire magnetic module / exterior electric circuit for supplying the solenoid, as well as this one's geometrical configuration may also be modelled in the COMSOL programme, by coupling the models for simulating the magnetic field (AC/DC→ mf) to the model of exterior electric circuit (AC/DC →cir). This design can also be made in the MATLAB platform, by using the SIMULINK module – the SimCape sub-module (www.users.abo.fi). The latter one was preferred, owing to the authors' experience in this programme. The module is set forth in Figure 6. The solenoid supplying inverter is illustrated by the adjustable source of voltage set up at the 230 V voltage and the 400 Hz frequency, whereas the solenoid is represented by the following elements:

- resistor – coiling strength;
- electromagnetic converter – the number of loops of the solenoid;
- reluctance – the configuration (the geometrical sizes) and the material of which the solenoid core is made;
- reluctance 1 – the configuration and the material of which the steel baffle is made;
- reluctance 2 – the lid 2, made of steel;
- reluctance 3 the OL pipe.

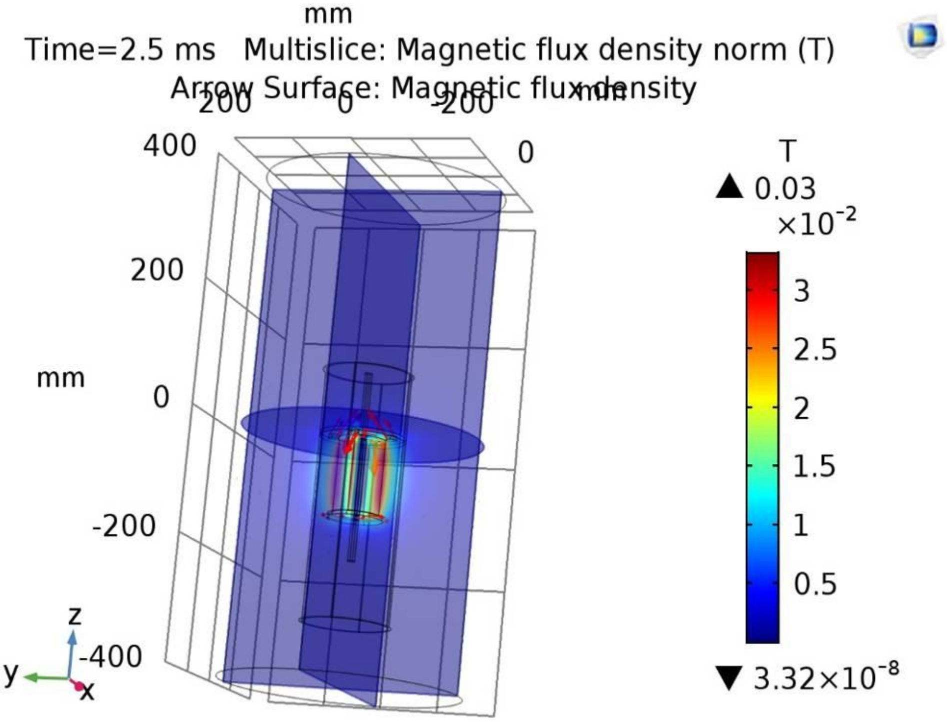

Figure 5. The intensity of the magnetic flow inside the magnetic module – a 3D model.

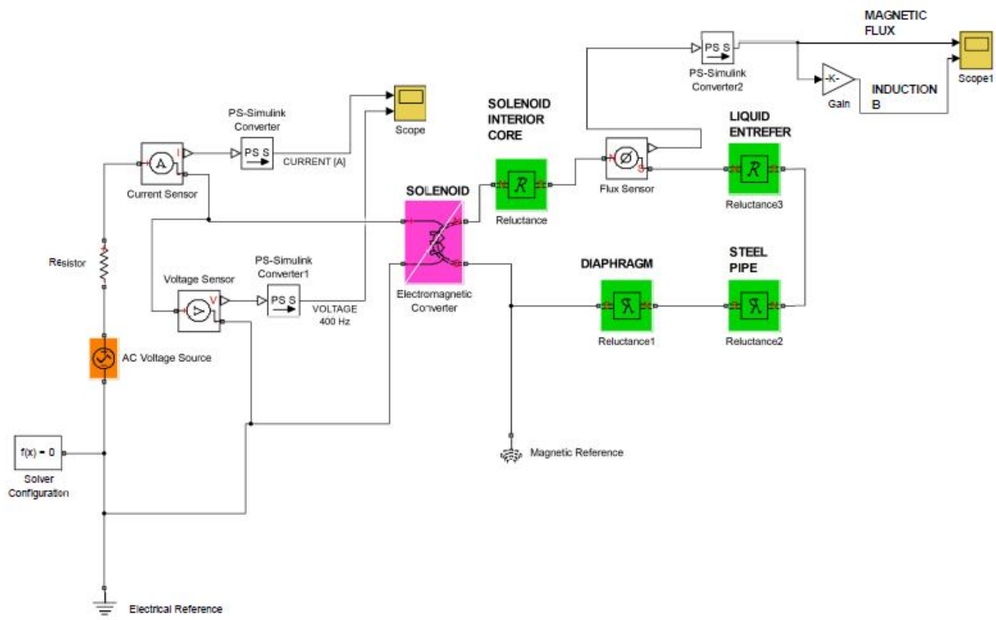

Figure 6. The SIMULINK model for checking up the magnetic mode.

The results achieved by running the model set out in Figure 6 are shown below, as follows: the solenoid supplying voltage and current (Figure 7), the magnetic flow and the magnetic induction (Figure 8).

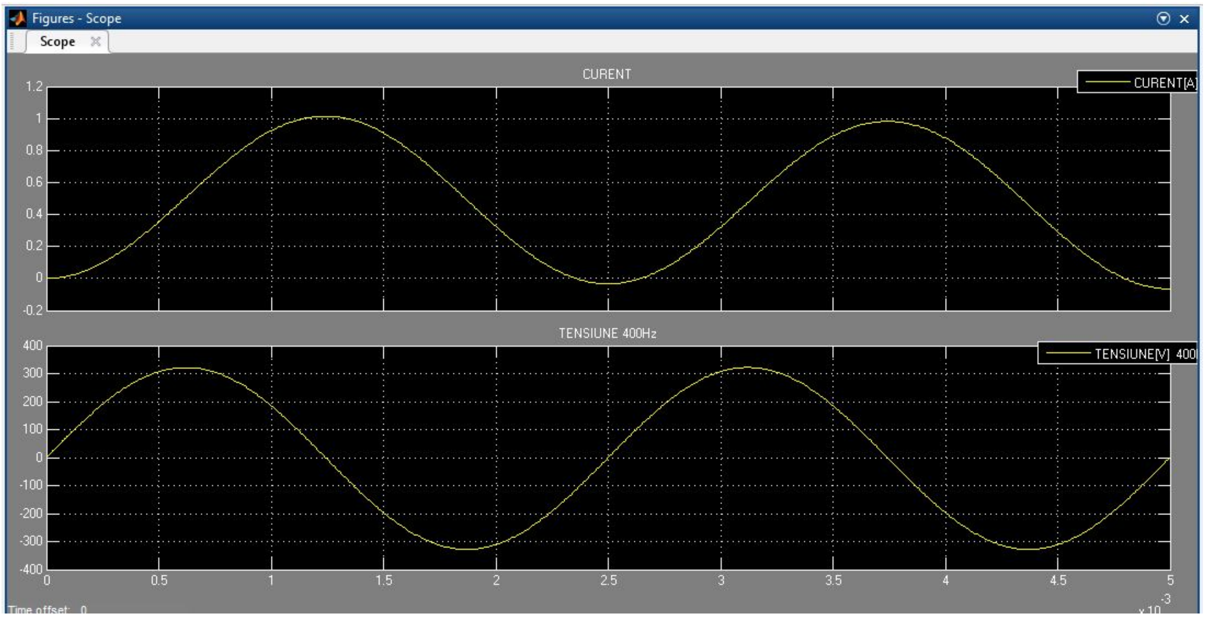

Figure 7. The solenoid supplying voltage and current – the SIMULINK model.

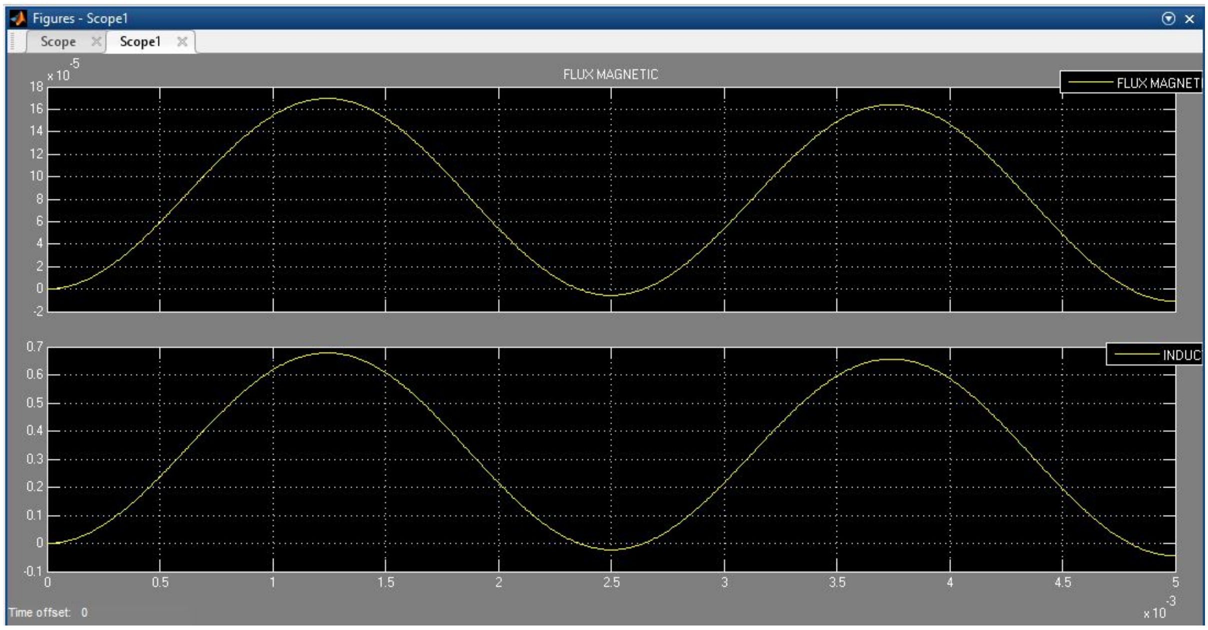

Figure 8. The magnetic flow and the magnetic induction in the magnetic module – the SIMULINK model.

Experimental results obtained by means of the magnetic module. The experiments performed in the magnetic module mainly aimed at the analysis of the target parameters (the parameters that have to be eliminated from the water), which are the following ones in our case : pH correction, iron, zinc, chrome, copper and nickel. The quality of the gross used water that enters the magnetic module is variable in time, because the circuit is closed, namely the treated water comes back in the same tank, from where the gross water is taken over and subjected to the treatment by the magnetic module. The following tests are made when the water enters in the purging module: pH, iron, zinc, copper, nickel, total chrome. The tests were carried out incessantly for one week and the module ran 4 h/day. The results are presented in Table 1 below.

Table 1
The value of the parameters that underwent analysis upon getting out of the purging module

Parameter	*The water upon entering the magnetic module*	*Day*				
		1	*2*	*3*	*4*	*5*
pH	7.79	8.2	7.9	8.1	8.3	8.7
Iron	873	485	98	9	3.6	1
Zinc	106	50	12	5	0.4	0.4
Copper	16	5	0.3	0.1	ND	ND
Chrome	10	5	2	0.2	0.1	0.1
Nickel	10	3.8	0.8	0.2	0.1	0.1

Conclusions. The experimental determinations carried out led to the following conclusions:

- the iron decrease from 4 g/l to 1 mg/l after passing twice through the SIMAG module;
- the zinc decrease under 1 mg/l;
- the chrome, the copper and the nickel drop under 0.5 mg/l;
- the experimental parameters obtained are in a good correlation with those designed and forecast for the plant;
- the analysis of the functional parameters shows that the SIMAG prototype reaches the performances for which it was created, namely, in our case, the reduction of the iron and of the heavy metals present in the water;
- the parameters of the water purged by means of the SIMAG module fall into the limits imposed by the NTPA002/2002 norm, so that the water may be discharged in the sewerage system.

References

***https://www.businesswire.com/news/home/20131112005843/en/Siemens-Introduces-CoMag%C2%AE-System-High-Rate-Clarification.
*** https://www.intechopen.com/books/waste-water-treatment-technologies-and-recent-analytical-developments/applications-of-magnetite-nanoparticles-for-heavy-metal-removal-from-wastewater.
***http://people.ee.ethz.ch/~fieldcom/ppscomsol/documents/User%20Guide/COMSOLMultiphysicsUsersGuide.pdf.
*** http://www.users.abo.fi/khaggblo/PDC/Using_Matlab_Simulink.pdf.

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